

PATENT ABSTRACTS OF JAPAN

(11)Publication number : 09-208932

(43)Date of publication of application : 12.08.1997

(51)Int.Cl.

C09K 3/10
C08J 9/06
// C08L 9:00

(21)Application number : 08-017738

(71)Applicant : TOKAI RUBBER IND LTD

(22)Date of filing : 02.02.1996

(72)Inventor : IKAGA SHIYUJI
MURAMATSU ATSUSHI

(54) EXPANDABLE RUBBER COMPOSITION FOR PACKING STRUCTURE AND FOAM FOR PACKING STRUCTURE

(57)Abstract:

PROBLEM TO BE SOLVED: To obtain an inexpensive and expandable rubber composition for packing a structure, excellent in storage stability and foam for packing a structure, having excellent compressive rigidity and large energy absorbing amount.

SOLUTION: This expandable rubber composition is arranged in a prescribed space in a structure and expanded by being heated to pack the space in the structure with the composition. The rubber composition is obtained by blending 100 pts.wt. diene-based rubber with 10-50 pts.wt. sulfur or 1-30 pts.wt. sulfur, 5-100 pts.wt. rigidity imparting agent and 5-40 pts.wt. foaming agent. This foam for packing a structure is obtained by heating and expanding the expandable rubber composition and has ≥ 0.5 kN/mm/25cm² area compressive rigidity and ≥ 100 kN.mm/25m² energy absorption amount.

LEGAL STATUS

[Date of request for examination] 28.09.2001

[Date of sending the examiner's decision of rejection] 09.03.2004

[Kind of final disposal of application other than the examiner's decision of rejection or application converted registration]

[Date of final disposal for application]

[Patent number]

[Date of registration]

[Number of appeal against examiner's decision of rejection]

[Date of requesting appeal against examiner's decision of rejection]

[Date of extinction of right]

CLAIMS

[Claim(s)]

[Claim 1] The fizz rubber constituent for structure restoration which is a fizz rubber constituent which is made to arrange by the predetermined opening in the structure, foams by being heated, and is filled up with the opening in this structure, and is characterized by coming to blend the sulfur of 10 - 50 weight section, and the foaming agent of 5 - 40 weight section to the 100 weight sections of diene system rubber.

[Claim 2] The fizz rubber constituent for structure restoration which is a fizz rubber constituent which is made to arrange by the predetermined opening in the structure, foams by being heated, and is filled up with the opening in this structure, and is characterized by coming to blend the rigid grant agent of the sulfur of 1 - 30 weight section, and the 5 - 100 weight section, and the foaming agent of 5 - 40 weight section to the 100 weight sections of diene system rubber.

[Claim 3] The compression rigidity which heated the fizz rubber constituent which comes to blend the sulfur of 10 - 50 weight section and the foaming agent of 5 - 40 weight section, it was made to foam to the diene system rubber of the 100 weight sections, and was acquired is 2.25cm. It is a 0.5 kN/mm [more than] hit, and the amount of energy-absorbing is 2.25cm. Foam for structure restoration characterized by being 100 or more kN-mm of hits.

[Claim 4] The compression rigidity which heated the fizz rubber constituent which comes to blend the rigid grant agent of the sulfur of 1 - 30 weight section and the 5 - 100 weight section and the foaming agent of 5 - 40 weight section, it was made to foam to the diene system rubber of the 100 weight sections, and was acquired is 2.25cm. It is a 0.5 kN/mm [more than] hit, and the amount of energy-absorbing is 2.25cm. Foam for structure restoration characterized by being 100 or more kN-mm of hits.

[Translation done.]

[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to the foam for structure restoration which can start the fizz rubber constituent for structure restoration, and the foam for structure restoration, especially can be advantageously obtained by heating the fizz rubber constituent for structure restoration which is low cost and was excellent in storage stability, and such a fizz rubber constituent, and foaming to them and which has the outstanding rigidity.

[0002]

[Background of the Invention] When a cavity was located in the interior of frame members (structure), such as a front pillar of an automobile, and a center pillar, and a wind generally passed through the inside of the cavity, the whizzing sound occurred or it was transmitted to such a cavernous part, and the engine oscillating sound was transmitted to in the car, and caused noise in the car, then, the thing for which the opening part of the structures, such as said frame member leading to the noise in the car, is filled up with foam from the former — passage of a wind, and transfer of an oscillating sound — controlling — with — **** — a cure, such as aiming at improvement in insulation, is taken.

[0003] and as an approach of filling up such an opening with foam The approach of inserting in the opening section the foam formed according to the configuration of an opening from an activity hole or the fizz constituent with which it foams with heating and the volume expands is processed in the shape of a sheet as a spot sealant. Make it filled up, arrange in an opening, it is made to foam with heating in the printing furnace of electropainting etc., and various technique, such as an approach filled up with the opening section, is adopted.

[0004] However, since the approach of inserting foam in the opening section is inserted from an activity hole, it is difficult for dispersion to arise to restoration nature and to be completely filled up in accordance with the configuration of the opening section to all the corners. And since the activity hole serves as a punching edge of a steel plate, an operator has the danger of damaging a hand.

[0005] Moreover, it not only improves the conventional noise in the car, but by recent years, it is coming as like that restoration of the foam to the structure is performed by the purpose which makes the reinforcement of the structure improve. And in order to acquire high rigidity, the fizz constituent which consists of an epoxy resin is used for such a fizz constituent for structure restoration. However, the shaping sheet of the fizz constituent which costs of an epoxy resin including a cross linking agent are high, and generally consists of such an epoxy resin Even if not heated, from the place currently formed in the state of the condition after adding a curing agent to an epoxy resin, and the so-called B stage under about 40-degrees C temperature conditions In order that a reaction might progress rapidly and might harden automatically (automatically) with the steam in an ambient atmosphere, it had the problem that storage stability was missing. So, in the cool place, after dedicating silica gel into the bag put in and sealed, it was fully careful of the fizz constituent which consists of such an epoxy resin, and it had to be saved, and the handling was very troublesome.

[0006]

[Problem(s) to be Solved] While succeeding in this invention against the background of this situation, and the place made into the solution technical problem being in here to offer the fizz rubber constituent for structure restoration which is low cost and is moreover excellent in storage stability and having high compression rigidity, it is also in offering the foam for structure restoration with many amounts of energy-absorbing.

[0007]

[Means for Solution] And that such a technical problem should be solved, this invention is made to arrange by the predetermined opening in the structure, and it foams to it by being heated. It is the fizz rubber constituent filled up with the opening in this structure, and let the fizz rubber constituent for structure restoration characterized by coming to blend the sulfur of 10 - 50 weight section, and the foaming agent of 5 - 40 weight section be the summary to the 100 weight sections of diene system rubber.

[0008] Moreover, it is made to arrange this invention by the predetermined opening in the structure, and foams by being heated. Are the fizz rubber constituent filled up with the opening in this structure, and the 100 weight sections of diene system rubber are received. Also let the fizz rubber constituent for structure restoration characterized by coming to blend the rigid grant agent of the sulfur of 1 - 30 weight section, and the 5 - 100 weight section, and the foaming agent of 5 - 40 weight section be the summary.

[0009] That is, if it is in the fizz rubber constituent for structure restoration according to this invention, using diene system rubber as a principal component, to it, it is the purpose which raises the rigidity of the foam which can obtain the sulfur of a predetermined rate or the sulfur of a predetermined rate, and a rigid grant agent, and is characterized [big] by making it blend. And although sulfur is used as a cross linking agent from the place which has adopted the rubber ingredient which consists of diene system rubber as a principal component, the fizz rubber constituent for structure restoration obtained can be made cheap from the place which is cheap as for such a rubber ingredient and sulfur. Moreover, even if it saves the rubber ingredient adopted in this invention in the condition of having made the sulfur which is a cross linking agent blend, unless it is made to heat, a very troublesome store method does not need to be used for it from the place which has the storage stability which did not harden automatically and was excellent like [in the case of the fizz constituent using the conventional epoxy resin].

[0010] And from the place which inherits and has the property of rubber, with the elasticity originating in rubber, the foam which heat this fizz rubber constituent, it is made to foam, and is obtained will have the outstanding toughness, and will have the absorption property of bigger striking energy from conventional foam.

[0011] And since it becomes the thing excellent in the rigidity of the foam which heat it, it is made to foam according to an operation of a rigid grant agent, and is obtained in adopting as the sulfur of a cross linking agent the configuration which uses a rigid grant agent together, there is the description which can reduce the amount of sulfur to add.

[0012] Moreover, for this invention, the compression rigidity like the above which heated the fizz rubber constituent which comes to blend the sulfur of 10 - 50 weight section and the foaming agent of 5 - 40 weight section, it was made to foam to the diene system rubber of the 100 weight sections, and was acquired is 2.25cm. It is a 0.5 kN/mm [more than] hit, and the amount of energy-absorbing is 2.25cm. Let the foam for structure restoration characterized by be 100 or more kN-mm of hits be the summary.

[0013] This invention receives the diene system rubber of the 100 weight sections. Furthermore, the sulfur of 1 - 30 weight section, The fizz rubber constituent which comes to blend the rigid grant agent of the 5 - 100 weight section and the foaming agent of 5 - 40 weight section is heated. The compression rigidity which was made to foam and was acquired is 2.25cm. It is a 0.5 kN/mm [more than] hit, and the amount of energy-absorbing is 2.25cm. Also let the foam for structure restoration characterized by being 100 or more kN-mm of hits be the summary.

[0014] By heating the fizz rubber constituent for structure restoration which has the aforementioned outstanding property, and making it foam, if it is in the foam for structure restoration according to this invention like the above in short, it is obtained easily and the compression rigidity of such foam is 2.25cm. It is a 0.5 kN/mm [more than] hit, and the amount of energy-absorbing is 2.25cm. It is 100 or more kN-mm of hits, and has the outstanding rigid and big amount of energy-absorbing.

[0015]

[Embodiment of the Invention] by the way, any of diene system rubber well-known [such as natural rubber (NR), butadiene rubber (BR), and a styrene butadiene rubber (SBR),] as diene system rubber used in the fizz rubber constituent for structure restoration according to this invention, or the foam for structure restoration -- although -- even if it is usable and is those blend objects, it does not interfere at all.

[0016] It is what is added in order that sulfur may raise the rigidity of the foam which heats a fizz rubber constituent, is made to foam according to the bridge formation operation which it has, and is obtained. Moreover, the amount used When a rigid grant agent is not made to blend, only by bridge formation with sulfur. In order to have to raise rigidity, you need to be made to blend in more amounts, and when a rigid grant agent is made to blend, on the other hand, it becomes enough [little combination] from the place which does not need to raise rigidity only by bridge formation with sulfur.

[0017] That is, when a rigid grant agent is not made to blend, it needs to be made to blend sulfur at a rate of 10 - 50 weight section to the 100 weight sections of diene system rubber. It is **, and is because the crosslinking density of the foam obtained will become inadequate if there is less this blending ratio of coal than 10 weight sections, so rigidity becomes low too much, and is because the crosslinking density of the foam obtained becomes large too much when there is more this blending ratio of coal than 50 weight sections, so foaming [of a rubber constituent] becomes inadequate.

[0018] On the other hand, when a rigid grant agent is made to blend, let sulfur be the blending ratio of coal of 1 - 30 weight section to the 100 weight sections of diene system rubber. In this case, if the sulphuric blending ratio of coal becomes less than 1 weight section, problems, like the rigidity of the foam obtained becomes inadequate, and when [than this rate] more, the rigidity of the foam obtained becomes high too much, and foam becomes weak will be caused.

[0019] Moreover, it is added in order to give rigidity to the foam which heat a fizz rubber constituent, it is made to foam and is obtained, and the aforementioned rigid grant agent can reduce a sulphuric content by addition of this rigid grant agent. And as an example of such a rigid grant agent, thermosetting resin, its denaturation objects, etc., such as phenol resin, an epoxy resin, melamine resin, and urethane resin, can be mentioned. And it is made for the blending ratio of coal of such a rigid grant agent to serve as the 5 - 100 weight section to the 100 weight sections of diene system rubber. It is **, and is because an operation of a rigid grant agent must fully have been demonstrated when there is less this blending ratio of coal than 5 weight sections, and is because the rigidity of the foam obtained becomes high too much and is not desirable, when there is more this blending ratio of coal than the 100 weight sections. In addition, in order to raise an operation of this rigid grant agent further, to thermosetting resin, curing agents, such as a hexamine, may be added in about 20 - 30% of rate of the theoretical equimolecular amount of resin, and it can also raise rigidity still more advantageous.

[0020] Furthermore, although it is added and a well-known thing may be suitably adopted from the former so that foam may be formed by decomposing and emitting gases, such as a carbon dioxide and nitrogen gas, when a rubber constituent is heated, the foaming agent used for this invention As an example of such a foaming agent, a sodium hydrogencarbonate, an ammonium carbonate, The thing of organic systems, such as a thing of inorganic systems, such as an ammonium hydrogencarbonate, and a diazo amino derivative, an azonitrile system, an azo dicarboxylic acid derivative, dinitrosopentamethylenetetramine, can be mentioned. And it is made to add this foaming agent by the blending ratio of coal of 5 - 40 weight section to the 100 weight sections of diene system rubber. It is **, and is because foaming operation sufficient when there is less this blending ratio of coal than 5 weight sections must have been demonstrated, and is because much more foaming operation is not necessarily demonstrated when [than 40 weight sections] more.

[0021] in addition, to the fizz rubber constituent for structure restoration according to this invention The various compounding agents known from the former besides the above mentioned diene system rubber, sulfur, the rigid grant agent, and the foaming agent, For example, it cannot be overemphasized that it is added if needed, and they do not interfere at all in the range in which neither of those things checks the purpose of this invention even if a vulcanization accelerator, a vulcanization assistant, processing aid, a bulking agent, etc. are blended as usual. For example, metallic oxides, such as a zinc oxide, are used and it is made to blend at a rate of 3 - 15 weight section extent to the 100 weight sections of diene system rubber as a vulcanization assistant generally. Moreover, fatty acids, such as stearic acid, are used at a rate of 0.5 - 5 weight section extent to the 100 weight sections of diene system rubber as processing aid. Furthermore, as a softener, there are process oil and the ester system plasticizer of liquid rubber, paraffin series, a naphthene, and an aroma system, it is used at a rate of 0 - 100 weight section extent to the 100 weight sections of diene system rubber, and a calcium carbonate, carbon black, a silica, talc, etc. are used in the rate of 0 - 150 weight section extent as a bulking agent further again to the 100 weight sections of diene system rubber.

[0022] And the fizz rubber constituent for structure restoration according to this invention will be prepared by blending a foaming agent with the sulfur of the specified quantity or sulfur and a rigid grant agent, and a list, and making the various compounding agents like the above blend further to a diene system rubber ingredient according to the same mixed technique as usual.

[0023] Moreover, the foam for structure restoration according to this invention can be easily obtained by heating the fizz rubber constituent for structure restoration according to this invention prepared like the above. That is, if said fizz rubber constituent for structure restoration is made to heat, easily, it will foam to it, it will be hardened and will serve as target foam. And in that case, it sets to the foam for structure restoration obtained, and the compression rigidity is 2.25cm. It is a 0.5 kN/mm [more than] hit, and the amount of energy-absorbing is 2.25cm. Heating conditions are selected and it is made to foam and harden so that it may become 100 or more kN-mm of hits. Generally, it is 160-210-degree C temperature conditions, and, more specifically, is heated about 15 to 30 minutes.

[0024] With by the way, the compression rigidity said by this invention In case one side compresses the field of the pair of the foam test piece formed in the cube which is 5cm, so that it may be compressed by part for 20mm/in the compression direction The value which imposed the compressive load P, asked for the relation between amount of displacement S in that case and said compressive-load P, and *(ed) and calculated early load fine variation (delta P) by early displacement fine variation (delta S) is meant, and it is it 25cm of test pieces 2 It expresses with the value of a hit. moreover, the time of performing compression like the above to the aforementioned foam test piece with the amount of absorbed energies said by this invention -- compression of compression initiation

to a test piece -- the amount of energy absorbed by the test piece by the time the variation rate was set to 30mm -- meaning --
**** -- it -- test piece 25cm² per -- it expresses with the value. Specifically, it is said amount of displacement:S and compressive
load :P Although the graph which showed the relation of ** is shown in drawing 1 in this graph, compression rigidity is the inclination
(deltaP/deltaS) of the standup in early stages of the related curve of amount of displacement:S, and compressive-load:P. Moreover,
the amount of absorbed energies compressive-load: -- P and a variation rate -- amount: --- it is the area (black painting part in
drawing 1) surrounded between the related curve with S, and the x axis (0-30mm).

[0025] And that compression rigidity is large means that the rigidity of foam is high, and that the amount of energy-absorbing is large
means that foam cannot be crushed easily, when the force of the same amount of energy as foam is added.

[0026] Therefore, when it is applied to the structures, such as a frame of an automobile, from the place which is what is strong against
an impact and is hard to be crushed, a passenger's safety is made to improve effectively from the place which will absorb the impact by
the automobile accident advantageously by the foam for structure restoration according to this invention.

[0027] Incidentally, in actually applying the foam for structure restoration according to this invention to the structure of an automobile
First, since it passes processes of the usual automobile manufacture, such as welding, cleaning and washing, and electrodeposition,
after arranging the structure fizz rubber constituent processed in the shape of a sheet on a location fixed target in the internal opening
of the structure, it sets at processes, such as paint printing. It is not necessary to establish a special heating process at all by being
heated from the place which is the thing you are made to foam and harden.

[0028]

[Example] It is a place needless to say that this invention is not what also receives any constraint by the publication of such an
example although the typical example of this invention is shown, in order to clarify this invention still more concretely below. Moreover,
it should be understood that it is what can add modification which becomes various based on this contractor's knowledge, correction,
amelioration, etc. to this invention unless it deviates from the meaning of this invention besides the following examples besides the
further above-mentioned concrete description.

[0029] First, the various fizz rubber constituents for structure restoration which have the *** presentation shown in the following
table 1 were prepared. Moreover, the stearic acid:1 weight section, the whiting:20 weight section, and the process oil:5 weight section
blend with the zinc-oxide:5 weight section as a vulcanization assistant, and that other than the component shown in this table 1 are
made to blend with a class product as processing aid. In addition, process oil came to add process oil to the rubber constituent of the
example 5 of this invention at the rubber constituent of the examples 1-3 of this invention at the rubber constituent of the example 4
of this invention, and the examples 1-2 of a comparison using the process oil of an aroma system using the process oil of a naphthene.

[0030]

[Table 1]

表 1

		本 発 明 例					比 較 例	
		1	2	3	4	5	1	2
成分組成 (重量部)	ジェン系 ゴム	A	100	100	100	—	—	—
		B	—	—	—	100	100	100
		C	—	—	—	50	50	50
	発 泡 剤	30	80	30	30	30	30	30
	イ オ ウ	20	20	1.5	10	20	2	5
	剛性付与剤	40	40	100	—	—	—	—
	フェノール系内部 添加型着色剤	—	—	—	—	—	—	—
	フェノール硬化剤	—	1.2	1.2	—	—	—	—
	カーボン FT	80	80	30	5	5	5	5
	加硫 促進剤	A	—	—	—	2.5	2.5	2.5
		B	—	—	—	0.2	0.2	0.2

ジェン系ゴム A: 中高ニトリルゴム
B: ハイスチレンゴム、C: スチレンゴム

発泡剤 : アゾジカルボンアミド系発泡剤

剛性付与剤 : カシュフェノールレジン

フェノール硬化剤 : ヘキサミン

加硫促進剤 A: チアゾール系加硫促進剤

B: テウラム系加硫促進剤

[0031] Subsequently, heated, the various fizz rubber constituents for structure restoration obtained above were made to foam by
holding for 20**2 minutes in the drying furnace adjusted to 180**2 degrees C, and the foam corresponding to each was obtained. And
these expansion ratio and block physical properties of foam that were acquired were investigated, and that result was shown in the

following table 2. In addition, it investigated [expansion ratio] also about the monograph affair for [160 degree-Cx] 20 minutes and for [215 degree-Cx] 20 minutes. Moreover, it investigated about vulcanization speed. And the result was combined and shown in the following table 2.

[0032] In addition, vulcanization speed calculated the value in 10% torque (T10) of the maximum torque, and the value in 90% torque (T90) of the maximum torque using the 180 degrees C [by the Monsanto rheometer] vulcanization curve.

[0033] Moreover, expansion ratio is 200mmx300mm magnitude about each fizz rubber constituent. On the fuel-level steel plate whose thickness is 0.8mm, in 100mmx100mm magnitude After thickness fabricated in the shape of [which is 5mm] a sheet, in the drying furnace adjusted to predetermined temperature, it measured by carrying out predetermined time maintenance by making it heat and foam and harden and asking for the scale factor (%) of the maximum sheet thickness after foaming to the sheet thickness before foaming.

[0034] Furthermore, you make it foam and harden by holding block physical properties for 20**2 minutes in the drying furnace which adjusted the fizz rubber constituent to 180**2 degrees C, and it was made for the obtained foam to serve as a test piece of a 50x50x50mm cube. Next, the autograph which attached the even steel plate which has thickness sufficient in the magnitude of 50x50mm or more is prepared. Using this, the field of a pair was compressed in the direction perpendicular to the field for said obtained test piece the rate for 20mm/, the amount of displacement in that case was taken along the axis of abscissa (x axis), the compressive load was taken along the axis of ordinate (y-axis), and those related curves were obtained as a graph (refer to drawing 1). and the compressive load which makes the inclination of the standup curve in early stages of compression the value of compression rigidity, and is shown with said related curve from the graph -- a variation rate -- amount (x) -- the variation rate from 0 (mm) -- amount (x) -- the area value (black painting part in drawing 1) integrated with and acquired to 30 (mm) was made into the amount of energy-absorbing.

[0035]

[Table 2]

表 2

		本 発 明 例					比 較 例	
		1	2	3	4	5	1	2
加硫速度 (秒)	T ₁₀	44	37	13	53	61	63	61
	T ₉₀	226	221	125	139	217	922	121
発泡倍率(%)	180℃×20分	176	141	141	162	183	254	290
	180℃×20分	323	269	161	344	373	251	406
	215℃×20分	272	154	166	245	306	215	378
ブロック物性	比重	0.252	0.282	0.421	0.390	0.276	0.359	0.384
	圧縮剛性*	0.32	0.75	2.91	0.69	1.12	0.23	0.41
	エネルギー吸収量**	203.0	151.4	305.5	110.6	242.4	54.5	75.9

* 1 : 単位 kN/mm

* 2 : 単位 kN・mm

[0036] Its amount of energy-absorbing is very big while the foam for structure restoration according to this invention has the outstanding compression rigidity, so that clearly from the result shown in this table 2. It was presupposed to it that the compression rigidity of the foam obtained from the fizz constituent of the example of a comparison was also small, its amount of energy-absorbing was small, and the predominance of the fizz rubber constituent for structure restoration and the foam for structure restoration according to this invention was clear.

[0037]

[Effect of the Invention] While cost may be advantageously reduction-ized according to the fizz rubber constituent for structure restoration according to this invention so that clearly also from the above explanation, the outstanding storage stability is acquired. And the handling becomes very easy by having the storage stability excellent in the fizz rubber constituent such.

[0038] Like the conventional epoxy resin fizz constituent, before heating, a reaction advances automatically, and it seems moreover, for foaming not to become inadequate in case the fizz rubber constituent for structure restoration according to this invention is filled up with the structure by having the outstanding storage stability using it.

[0039] Furthermore, it sets to the foam for structure restoration according to this invention, and the compression rigidity is 2 25cm. It is a 0.5 kN/mm hit, and the amount of energy-absorbing is 2 25cm. A passenger's safety may be made to improve effectively, when the big impact can be absorbed and such foam for structure restoration is applied to an automobile, while having high rigidity from the place which is 100 or more kN-mm of hits.

[Translation done.]

TECHNICAL FIELD

[Field of the Invention] This invention relates to the foam for structure restoration which can start the fizz rubber constituent for structure restoration, and the foam for structure restoration, especially can be advantageously obtained by heating the fizz rubber constituent for structure restoration which is low cost and was excellent in storage stability, and such a fizz rubber constituent, and foaming to them and which has the outstanding rigidity.

[Translation done.]

PRIOR ART

[Background of the Invention] When a cavity was located in the interior of frame members (structure), such as a front pillar of an automobile, and a center pillar, and a wind generally passed through the inside of the cavity, the whizzing sound occurred or it was transmitted to such a cavernous part, and the engine oscillating sound was transmitted to in the car, and caused noise in the car. then, the thing for which the opening part of the structures, such as said frame member leading to the noise in the car, is filled up with foam from the former — passage of a wind, and transfer of an oscillating sound — controlling — with — **** — a cure, such as aiming at improvement in insulation, is taken.

[0003] and as an approach of filling up such an opening with foam The approach of inserting in the opening section the foam formed according to the configuration of an opening from an activity hole or the fizz constituent with which it foams with heating and the volume expands is processed in the shape of a sheet as a spot sealant. Make it filled up, arrange in an opening, it is made to foam with heating in the printing furnace of electropainting etc., and various technique, such as an approach filled up with the opening section, is adopted.

[0004] However, since the approach of inserting foam in the opening section is inserted from an activity hole, it is difficult for dispersion to arise to restoration nature and to be completely filled up in accordance with the configuration of the opening section to all the corners. And since the activity hole serves as a punching edge of a steel plate, an operator has the danger of damaging a hand.

[0005] Moreover, it not only improves the conventional noise in the car, but by recent years, it is coming as like that restoration of the foam to the structure is performed by the purpose which makes the reinforcement of the structure improve. And in order to acquire high rigidity, the fizz constituent which consists of an epoxy resin is used for such a fizz constituent for structure restoration. However, the shaping sheet of the fizz constituent which costs of an epoxy resin including a cross linking agent are high, and generally consists of such an epoxy resin. Even if not heated, from the place currently formed in the state of the condition after adding a curing agent to an epoxy resin, and the so-called B stage under about 40-degree C temperature conditions. In order that a reaction might progress rapidly and might harden automatically (automatically) with the steam in an ambient atmosphere, it had the problem that storage stability was missing. So, in the cool place, after dedicating silica gel into the bag put in and sealed, it was fully careful of the fizz constituent which consists of such an epoxy resin, and it had to be saved, and the handling was very troublesome.

[Translation done.]

EFFECT OF THE INVENTION

[Effect of the Invention] While cost may be advantageously reduction-ized according to the fizz rubber constituent for structure restoration according to this invention so that clearly also from the above explanation, the outstanding storage stability is acquired. And the handling becomes very easy by having the storage stability excellent in the fizz rubber constituent such.

[0038] Like the conventional epoxy resin fizz constituent, before heating, a reaction advances automatically, and it seems moreover, for foaming not to become inadequate in case the fizz rubber constituent for structure restoration according to this invention is filled up with the structure by having the outstanding storage stability using it.

[0039] Furthermore, it sets to the foam for structure restoration according to this invention, and the compression rigidity is 2.25cm. It is a 0.5 kN/mm hit, and the amount of energy-absorbing is 2.25cm. A passenger's safety may be made to improve effectively, when the big impact can be absorbed and such foam for structure restoration is applied to an automobile, while having high rigidity from the place which is 100 or more kN-mm of hits.

[Translation done.]

TECHNICAL PROBLEM

[Problem(s) to be Solved] While succeeding in this invention against the background of this situation, and the place made into the solution technical problem being in here to offer the fizz rubber constituent for structure restoration which is low cost and is moreover excellent in storage stability and having high compression rigidity, it is also in offering the foam for structure restoration with many amounts of energy-absorbing.

[Translation done.]

MEANS

[Means for Solution] And that such a technical problem should be solved, this invention is made to arrange by the predetermined opening in the structure, and it foams to it by being heated. It is the fizz rubber constituent filled up with the opening in this structure, and let the fizz rubber constituent for structure restoration characterized by coming to blend the sulfur of 10 - 50 weight section, and the foaming agent of 5 - 40 weight section be the summary to the 100 weight sections of diene system rubber.

[0008] Moreover, it is made to arrange this invention by the predetermined opening in the structure, and foams by being heated. Are the fizz rubber constituent filled up with the opening in this structure, and the 100 weight sections of diene system rubber are received. Also let the fizz rubber constituent for structure restoration characterized by coming to blend the rigid grant agent of the sulfur of 1 - 30 weight section, and the 5 - 100 weight section, and the foaming agent of 5 - 40 weight section be the summary.

[0009] That is, if it is in the fizz rubber constituent for structure restoration according to this this invention, using diene system rubber as a principal component, to it, it is the purpose which raises the rigidity of the foam which can obtain the sulfur of a predetermined rate or the sulfur of a predetermined rate, and a rigid grant agent, and is characterized [big] by making it blend. And although sulfur is used as a cross linking agent from the place which has adopted the rubber ingredient which consists of diene system rubber as a principal component, the fizz rubber constituent for structure restoration obtained can be made cheap from the place which is cheap as for such a rubber ingredient and sulfur. Moreover, even if it saves the rubber ingredient adopted in this invention in the condition of having made the sulfur which is a cross linking agent blend, unless it is made to heat, a very troublesome store method does not need to be used for it from the place which has the storage stability which did not harden automatically and was excellent like [in the case of the fizz constituent using the conventional epoxy resin].

[0010] And from the place which inherits and has the property of rubber, with the elasticity originating in rubber, the foam which heat this fizz rubber constituent, it is made to foam, and is obtained will have the outstanding toughness, and will have the absorption property of bigger striking energy from conventional foam.

[0011] And since it becomes the thing excellent in the rigidity of the foam which heat it, it is made to foam according to an operation of a rigid grant agent, and is obtained in adopting as the sulfur of a cross linking agent the configuration which uses a rigid grant agent together, there is the description which can reduce the amount of sulfur to add.

[0012] Moreover, for this invention, the compression rigidity like the above which heated the fizz rubber constituent which comes to blend the sulfur of 10 - 50 weight section and the foaming agent of 5 - 40 weight section, it was made to foam to the diene system rubber of the 100 weight sections, and was acquired is 2 25cm. It is a 0.5 kN/mm [more than] hit, and the amount of energy-absorbing is 2 25cm. Let the foam for structure restoration characterized by be 100 or more kN-mm of hits be the summary.

[0013] This invention receives the diene system rubber of the 100 weight sections. Furthermore, the sulfur of 1 - 30 weight section, The fizz rubber constituent which comes to blend the rigid grant agent of the 5 - 100 weight section and the foaming agent of 5 - 40 weight section is heated. The compression rigidity which was made to foam and was acquired is 2 25cm. It is a 0.5 kN/mm [more than] hit, and the amount of energy-absorbing is 2 25cm. Also let the foam for structure restoration characterized by being 100 or more kN-mm of hits be the summary.

[0014] By heating the fizz rubber constituent for structure restoration which has the aforementioned outstanding property, and making it foam, if it is in the foam for structure restoration according to this invention like the above in short, it is obtained easily and the compression rigidity of such foam is 2 25cm. It is a 0.5 kN/mm [more than] hit, and the amount of energy-absorbing is 2 25cm. It is 100 or more kN-mm of hits, and has the outstanding rigid and big amount of energy-absorbing.

[0015]

[Embodiment of the Invention] by the way, any of diene system rubber well-known [such as natural rubber (NR), butadiene rubber (BR), and a styrene butadiene rubber (SBR),] as diene system rubber used in the fizz rubber constituent for structure restoration according to this invention, or the foam for structure restoration -- although -- even if it is usable and is those blend objects, it does not interfere at all.

[0016] It is what is added in order that sulfur may raise the rigidity of the foam which heats a fizz rubber constituent, is made to foam according to the bridge formation operation which it has, and is obtained. Moreover, the amount used When a rigid grant agent is not made to blend, only by bridge formation with sulfur In order to have to raise rigidity, you need to be made to blend in more amounts, and when a rigid grant agent is made to blend, on the other hand, it becomes enough [little combination] from the place which does not need to raise rigidity only by bridge formation with sulfur.

[0017] That is, when a rigid grant agent is not made to blend, it needs to be made to blend sulfur at a rate of 10 - 50 weight section to the 100 weight sections of diene system rubber. It is **, and is because the crosslinking density of the foam obtained will become inadequate if there is less this blending ratio of coal than 10 weight sections, so rigidity becomes low too much, and is because the crosslinking density of the foam obtained becomes large too much when there is more this blending ratio of coal than 50 weight sections, so foaming [of a rubber constituent] becomes inadequate.

[0018] On the other hand, when a rigid grant agent is made to blend, let sulfur be the blending ratio of coal of 1 - 30 weight section to the 100 weight sections of diene system rubber. In this case, if the sulphuric blending ratio of coal becomes less than 1 weight section, problems, like the rigidity of the foam obtained becomes inadequate, and when [than this rate] more, the rigidity of the foam obtained becomes high too much, and foam becomes weak will be caused.

[0019] Moreover, it is added in order to give rigidity to the foam which heat a fizz rubber constituent, it is made to foam and is obtained, and the aforementioned rigid grant agent can reduce a sulphuric content by addition of this rigid grant agent. And as an example of such a rigid grant agent, thermosetting resin, its denaturation objects, etc., such as phenol resin, an epoxy resin, melamine resin, and urethane resin, can be mentioned. And it is made for the blending ratio of coal of such a rigid grant agent to serve as the 5 - 100 weight section to the 100 weight sections of diene system rubber. It is **, and is because an operation of a rigid grant agent must fully have been demonstrated when there is less this blending ratio of coal than 5 weight sections, and is because the rigidity of the foam obtained becomes high too much and is not desirable, when there is more this blending ratio of coal than the 100 weight sections. In addition, in order to raise an operation of this rigid grant agent further, to thermosetting resin, curing agents, such as a hexamine, may be added in about 20 - 30% of rate of the theoretical equimolecular amount of resin, and it can also raise rigidity still more advantageous.

[0020] Furthermore, although it is added and a well-known thing may be suitably adopted from the former so that foam may be formed by decomposing and emitting gases, such as a carbon dioxide and nitrogen gas, when a rubber constituent is heated, the foaming agent used for this invention As an example of such a foaming agent, a sodium hydrogencarbonate, an ammonium carbonate, The thing of organic systems, such as a thing of inorganic systems, such as an ammonium hydrogencarbonate, and a diazo amino derivative, an azonitrile system, an azo dicarboxylic acid derivative, dinitrosopentamethylenetetramine, can be mentioned. And it is made to add this foaming agent by the blending ratio of coal of 5 ~ 40 weight section to the 100 weight sections of diene system rubber. It is **, and is because foaming operation sufficient when there is less this blending ratio of coal than 5 weight sections must have been demonstrated, and is because much more foaming operation is not necessarily demonstrated when [than 40 weight sections] more.

[0021] in addition, to the fizz rubber constituent for structure restoration according to this invention The various compounding agents known from the former besides the above mentioned diene system rubber, sulfur, the rigid grant agent, and the foaming agent, For example, it cannot be overemphasized that it is added if needed, and they do not interfere at all in the range in which neither of those things checks the purpose of this invention even if a vulcanization accelerator, a vulcanization assistant, processing aid, a bulking agent, etc. are blended as usual. For example, metallic oxides, such as a zinc oxide, are used and it is made to blend at a rate of 3 ~ 15 weight section extent to the 100 weight sections of diene system rubber as a vulcanization assistant generally. Moreover, fatty acids, such as stearic acid, are used at a rate of 0.5 ~ 5 weight section extent to the 100 weight sections of diene system rubber as processing aid. Furthermore, as a softener, there are process oil and the ester system plasticizer of liquid rubber, paraffin series, a naphthene, and an aroma system, it is used at a rate of 0 ~ 100 weight section extent to the 100 weight sections of diene system rubber, and a calcium carbonate, carbon black, a silica, talc, etc. are used in the rate of 0 ~ 150 weight section extent as a bulking agent further again to the 100 weight sections of diene system rubber.

[0022] And the fizz rubber constituent for structure restoration according to this invention will be prepared by blending a foaming agent with the sulfur of the specified quantity or sulfur and a rigid grant agent, and a list, and making the various compounding agents like the above blend further to a diene system rubber ingredient according to the same mixed technique as usual.

[0023] Moreover, the foam for structure restoration according to this invention can be easily obtained by heating the fizz rubber constituent for structure restoration according to this invention prepared like the above. That is, if said fizz rubber constituent for structure restoration is made to heat, easily, it will foam to it, it will be hardened and will serve as target foam. And in that case, it sets to the foam for structure restoration obtained, and the compression rigidity is 2.25cm. It is a 0.5 kN/mm [more than] hit, and the amount of energy-absorbing is 2.25cm. Heating conditions are selected and it is made to foam and harden so that it may become 100 or more kN-mm of hits. Generally, it is 160~210-degree C temperature conditions, and, more specifically, is heated about 15 to 30 minutes.

[0024] With by the way, the compression rigidity said by this invention In case one side compresses the field of the pair of the foam test piece formed in the cube which is 5cm, so that it may be compressed by part for 20mm/in the compression direction The value which imposed the compressive load P, asked for the relation between amount of displacement:S in that case and said compressive-load:P, and ** (ed) and calculated early load fine variation (ΔP) by early displacement fine variation (ΔS) is meant, and it is it 25cm of test pieces 2 It expresses with the value of a hit. moreover, the time of performing compression like the above to the aforementioned foam test piece with the amount of absorbed energies said by this invention — compression of compression initiation to a test piece — the amount of energy absorbed by the test piece by the time the variation rate was set to 30mm — meaning — **** — it — test piece 25cm² per — It expresses with the value. Specifically, it is said amount of displacement:S and compressive load :P Although the graph which showed the relation of ** is shown in drawing 1. In this graph, compression rigidity is the inclination ($\Delta P/\Delta S$) of the standup in early stages of the related curve of amount of displacement:S, and compressive-load:P. Moreover, the amount of absorbed energies compressive-load: — P and a variation rate — amount: — it is the area (black painting part in drawing 1) surrounded between the related curve with S, and the x axis (0~30mm).

[0025] And that compression rigidity is large means that the rigidity of foam is high, and that the amount of energy-absorbing is large means that foam cannot be crushed easily, when the force of the same amount of energy as foam is added.

[0026] Therefore, when it is applied to the structures, such as a frame of an automobile, from the place which is what is strong against an impact and is hard to be crushed, a passenger's safety is made to improve effectively from the place which will absorb the impact by the automobile accident advantageously by the foam for structure restoration according to this invention.

[0027] Incidentally, in actually applying the foam for structure restoration according to this invention to the structure of an automobile First, since it passes processes of the usual automobile manufacture, such as welding, cleaning and washing, and electrodeposition, after arranging the structure fizz rubber constituent processed in the shape of a sheet on a location fixed target in the internal opening of the structure, it sets at processes, such as paint printing. It is not necessary to establish a special heating process at all by being heated from the place which is the thing you are made to foam and harden.

[0028]

[Translation done.]

EXAMPLE

[Example] It is a place needless to say that this invention is not what also receives any constraint by the publication of such an example although the typical example of this invention is shown, in order to clarify this invention still more concretely below. Moreover, it should be understood that it is what can add modification which becomes various based on this contractor's knowledge, correction, amelioration, etc. to this invention unless it deviates from the meaning of this invention besides the following examples besides the further above-mentioned concrete description.

[0029] First, the various fizz rubber constituents for structure restoration which have the *** presentation shown in the following table 1 were prepared. Moreover, the stearic acid:1 weight section, the whitening:20 weight section, and the process oil:5 weight section blend with the zinc-oxide:5 weight section as a vulcanization assistant, and that other than the component shown in this table 1 are made to blend with a class product as processing aid. In addition, process oil came to add process oil to the rubber constituent of the example 5 of this invention at the rubber constituent of the examples 1-3 of this invention at the rubber constituent of the example 4 of this invention, and the examples 1-2 of a comparison using the process oil of an aroma system using the process oil of a naphthene.

[0030]

[Table 1]

表 1

		本 発 明 例					比較例	
		1	2	3	4	5	1	2
成分組成 (重量部)	ジエン系 ゴム	A	100	100	100	—	—	—
		B	—	—	—	100	100	100
		C	—	—	—	50	50	50
	発泡剤	30	30	30	30	30	30	30
	イ オ ウ	20	20	1.5	10	20	2	5
	剛性付与剤	40	40	100	—	—	—	—
	フェノール系内部 添加型接着剤	—	—	—	—	—	—	—
	フェノール硬化剤	—	1.2	1.2	—	—	—	—
	カーボン FT	30	30	30	5	5	5	5
	加硫 促進剤	A	—	—	—	2.5	2.5	2.5
		B	—	—	—	0.2	0.2	0.2

ジエン系ゴム A:中低ニトリルゴム
B:ヘイスチレンゴム C:スチレンゴム

発泡剤 :アゾジカルボンアミド系発泡剤

剛性付与剤 :カシュフェノールレジン

フェノール硬化剤:ヘキサミン

加硫促進剤 A:チアゾール系加硫促進剤

B:チウラム系加硫促進剤

[0031] Subsequently, heated, the various fizz rubber constituents for structure restoration obtained above were made to foam by holding for 20**2 minutes in the drying furnace adjusted to 180**2 degrees C, and the foam corresponding to each was obtained. And these expansion ratio and block physical properties of foam that were acquired were investigated, and that result was shown in the following table 2. In addition, it investigated [expansion ratio] also about the monograph affair for [160 degree-Cx] 20 minutes and for [215 degree-Cx] 20 minutes. Moreover, it investigated about vulcanization speed. And the result was combined and shown in the following table 2.

[0032] In addition, vulcanization speed calculated the value in 10% torque (T10) of the maximum torque, and the value in 90% torque (T90) of the maximum torque using the 180 degrees C [by the Monsanto rheometer] vulcanization curve.

[0033] Moreover, expansion ratio is 200mmx300mm magnitude about each fizz rubber constituent. On the fuel-level steel plate whose thickness is 0.8mm, in 100mmx100mm magnitude After thickness fabricated in the shape of [which is 5mm] a sheet, in the drying furnace adjusted to predetermined temperature, it measured by carrying out predetermined time maintenance by making it heat and foam and harden and asking for the scale factor (%) of the maximum sheet thickness after foaming to the sheet thickness before foaming.

[0034] Furthermore, you make it foam and harden by holding block physical properties for 20**2 minutes in the drying furnace which adjusted the fizz rubber constituent to 180**2 degrees C, and it was made for the obtained foam to serve as a test piece of a 50x50x50mm cube. Next, the autograph which attached the even steel plate which has thickness sufficient in the magnitude of 50x50mm or more is prepared. Using this, the field of a pair was compressed in the direction perpendicular to the field for said obtained

test piece the rate for 20mm/, the amount of displacement in that case was taken along the axis of abscissa (x axis), the compressive load was taken along the axis of ordinate (y-axis), and those related curves were obtained as a graph (refer to drawing 1). and the compressive load which makes the inclination of the standup curve in early stages of compression the value of compression rigidity, and is shown with said related curve from the graph — a variation rate — amount (x) = — the variation rate from 0 (mm) — amount (x) = — the area value (black painting part in drawing 1) integrated with and acquired to 30 (mm) was made into the amount of energy-absorbing.

[0035]

[Table 2]

表 2

		本 発 明 例					比 較 例	
		1	2	3	4	5	1	2
加硫速さ (秒)	T ₁₀	44	37	13	53	61	68	61
	T ₉₀	226	221	126	199	217	322	121
発泡倍率(%)	160 °C×20分	176	141	141	162	188	254	200
	180 °C×20分	323	269	161	344	373	251	406
	215 °C×20分	272	154	166	245	306	215	378
ブロック物性	比 重	0.252	0.282	0.421	0.390	0.276	0.359	0.334
	圧縮剛性*	0.82	0.75	2.91	0.68	1.12	0.23	0.41
	エネルギー吸収量**	203.0	151.4	305.5	110.6	242.4	54.5	75.9

* 1 : 単位 kN/mm

* 2 : 単位 kN・mm

[0036] Its amount of energy-absorbing is very big while the foam for structure restoration according to this invention has the outstanding compression rigidity, so that clearly from the result shown in this table 2. It was presupposed to it that the compression rigidity of the foam obtained from the fizz constituent of the example of a comparison was also small, its amount of energy-absorbing was small, and the predominance of the fizz rubber constituent for structure restoration and the foam for structure restoration according to this invention was clear.

[Translation done.]

DESCRIPTION OF DRAWINGS

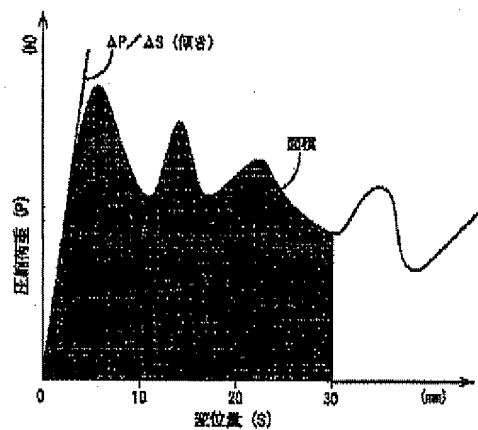
[Brief Description of the Drawings]

[Drawing 1] It is the graph which shows the relation of the amount of displacement and compressive load at the time of compressing the foam for structure restoration according to this invention.

[Translation done.]

DRAWINGS

[Drawing 1]



[Translation done.]